SEMICONDUCTOR PHYSICS LABORATORY
UNIVERSITY OF LEUVEN

# Interfaces and morphology of Si nanocrystals in $SiO/SiO_2$ superstructures

Mihaela JIVANESCU, prof. Andre Stesmans



## Outline

1. ESR active interface defects
2. $Si/SiO_2$ superstructures
3. ESR results
   – as received sample
   – irradiated sample
   – passivated sample
   – Ar-ion laser irradiation
4. Morphology
5. Conclusions

## Outline

1. ESR active interface defects
2. $Si/SiO_2$ superstructures
3. ESR results
   – as received sample
   – irradiated sample
   – passivated sample
   – Ar-ion laser irradiation
4. Morphology
5. Conclusions



## ESR active interface defects

$P_b$-type inherent defects

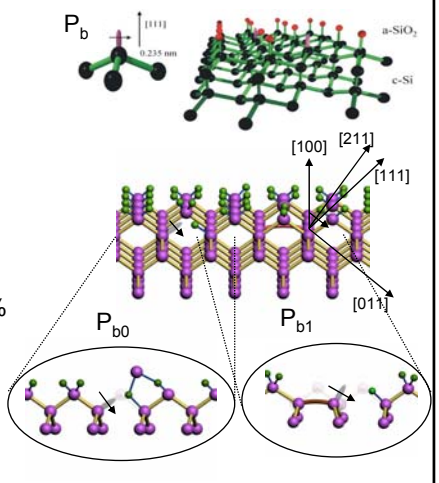
*Stesmans A. et al., Phys. Rev. B **58**, 15801 (1998).*

- Paramagnetic
- Coordination point defects
- Mismatch induced: *inherent*
- Density: *reproducible* (naturally determined)
  ($T_{ox}$ ~800 - 960 °C)

(111)$Si/SiO_2$: $P_b$ $[P_b] \sim 5x10^{12}$ $cm^{-2}$ ↔ f~0.6%
($N_a$ =7.83x$10^{14}$ $cm^{-2}$)

(100)$Si/SiO_2$: $P_{b0}$ $[P_{b0}] \sim 1x10^{12}$ $cm^{-2}$

$P_{b1}$ $[P_{b1}] \sim 1x10^{12}$ $cm^{-2}$



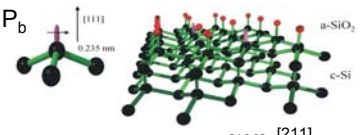

$P_b$-type defects indicate presence of facets

## ESR active interface defects

$P_b$-type inherent defects

*Stesmans A. et al., Phys. Rev. B **58**, 15801 (1998).*

- Thermochemical properties dominated by reversible $P_b$ interaction with hydrogen:



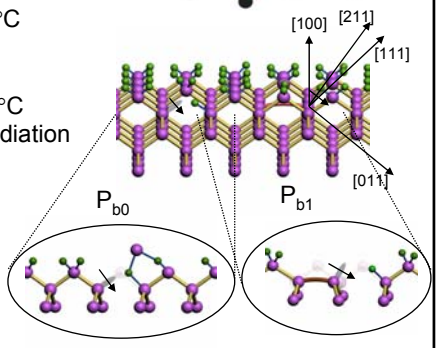

*Passivation*: pictured as

$P_b + H_2 \rightarrow P_bH + H$, $T \geq 220$ °C

*Dissociation*:

$P_bH \rightarrow P_b + H$, $T \geq 500$ °C

VUV irradiation




- Electrically: $P_b$, $P_{b0}$: detrimental amphoteric interface traps

Deep levels in Si bandgap: +/0: $E_v$ + 0.3 eV

0/-: $E_v$ + 0.8 eV

Recombination centers

*But*: NOT the only type of interface traps!

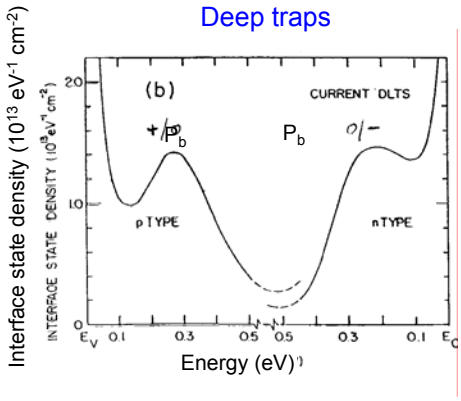


## ESR active interface defects

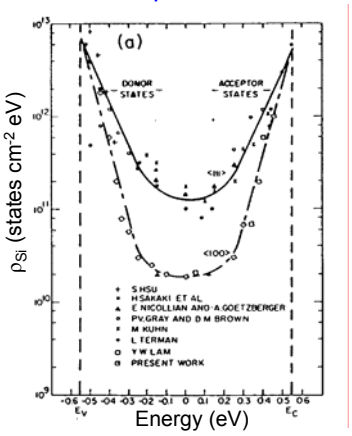
Levels in the Si bandgap

*Stesmans A. et al., Phys. Rev. B **58**, 15801 (1998).*

Deep traps




after passivation



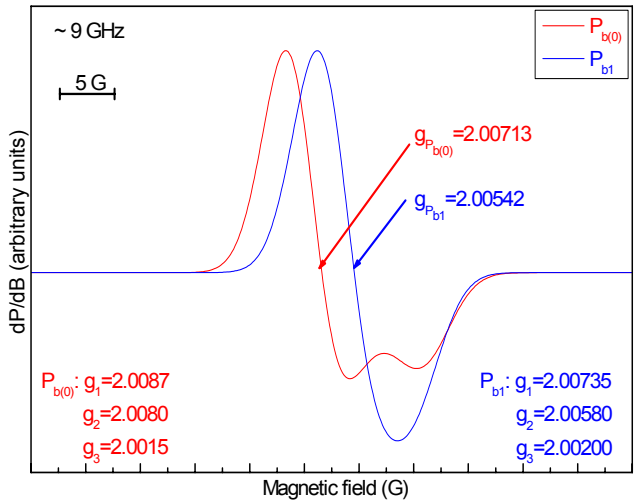

**As-grown thermal (111) $Si/SiO_2$**

$Si/SiO_2$: postmetallization anneal in forming gas (10% $H_2$ in $N_2$)

## ESR active interface defects

*Powder pattern* $P_b$-type centers

*Stesmans A., Afanas'ev V.V., J. Appl. Phys.* ***83****, 2449 (1998).*




Expected:
various orientations
of
the facets

Powder pattern $P_b$-type centers are used for simulations



## Outline

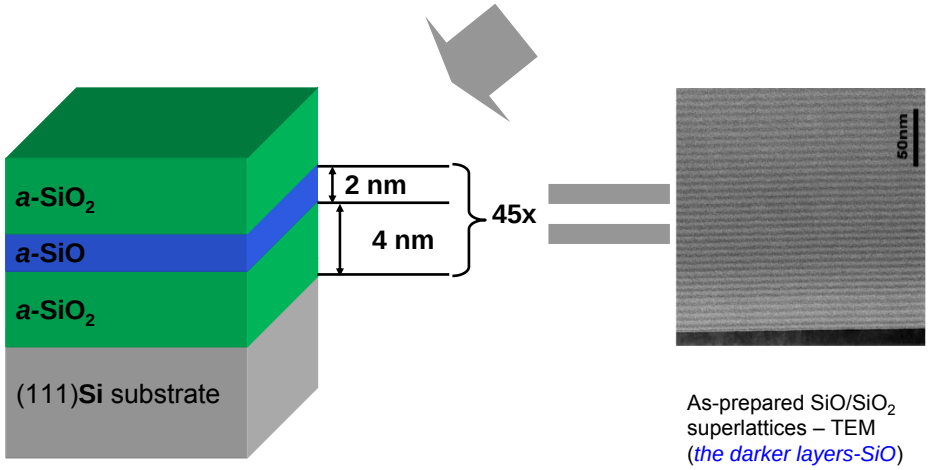
1. ESR active interface defects
2. $Si/SiO_2$ superstructures
3. ESR results
– as received sample
– irradiated sample
– passivated sample
– Ar-ion laser irradiation
4. Morphology
5. Conclusions

## Introduction

Preparation of the superlattice

*M. Zacharias et al., Appl. Phys. Lett.* ***80****, 661 (2002).*

***Reactive evaporation of SiO powders in oxygen atmosphere***



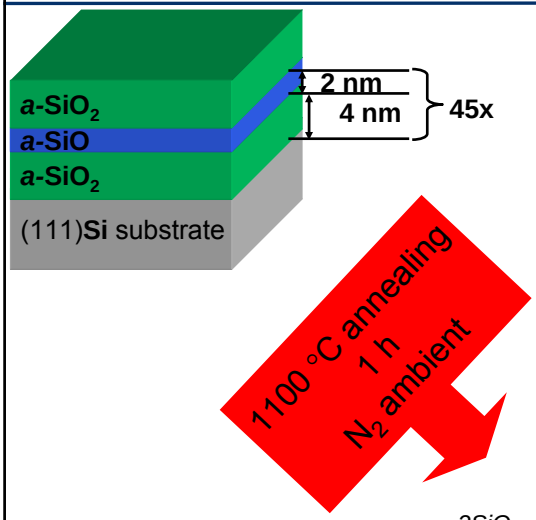

As-prepared $SiO/SiO_2$ superlattices – TEM (*the darker layers-SiO*)

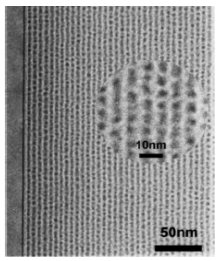


## Introduction

Preparation of the superlattice

*M. Zacharias et al., Appl. Phys. Lett.* ***80****, 661 (2002).*




HRTEM (*the crystals are only found in former SiO layers*)

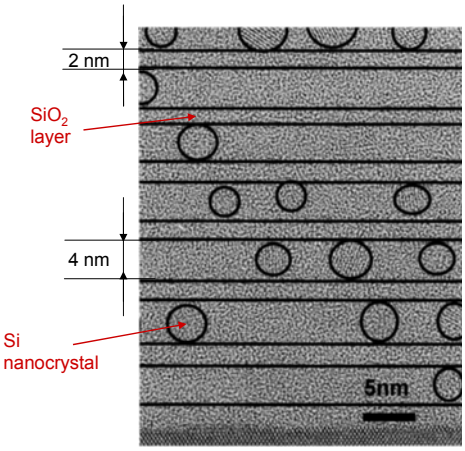
37 layers left

$2SiO \rightarrow SiO_2 + Si$

## Introduction

HRTEM of Si-nc

*M. Zacharias et al., Appl. Phys. Lett.* ***80****, 661 (2002).*




• HRTEM image of the film. For clarity, the visible nanocrystals are highlighted by circles.

• The crystals are only found in the former SiO layers, which is emphasized by the lines in the image



## Outline

1. ESR active interface defects
2. $Si/SiO_2$ superstructures
3. ESR results
   – as received sample
   – irradiated sample
   – passivated sample
   – Ar-ion laser irradiation
4. Morphology
5. Conclusions

## ESR

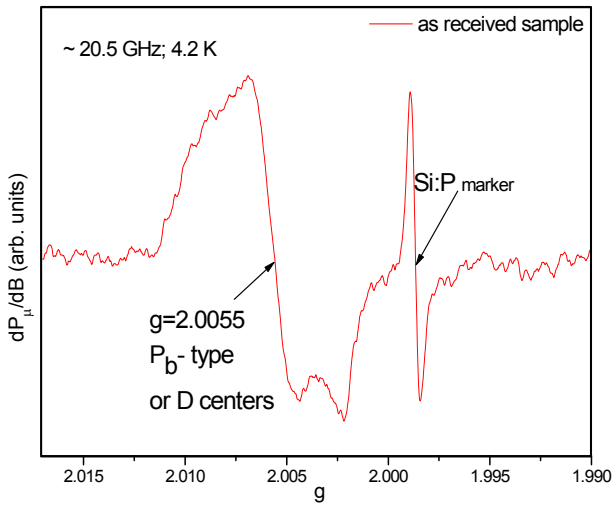


1. **High-sensitivity ESR**
   - 3 spectrometers:
     - X-band (~ 9 GHz) – local construction
     - K-band (~ 20.5 GHz) – local construction
       – sensitivity summum
     - Q-band (~ 34 GHz) – commercial
   - Low-T (4.2 K) observations
   - Defect density determination using markers (Si:P)
2. **Irradiations**
   - He-Cd laser – 325 nm
   - Xenon lamp – 180-1000 nm
   - VUV lamp – 123.6 nm
   - Ar-ion laser – 351-364 nm
     - used for PL measurements
3. **Passivation**
   - 1 atm pure $H_2$, 600°C, 30 min



## ESR results



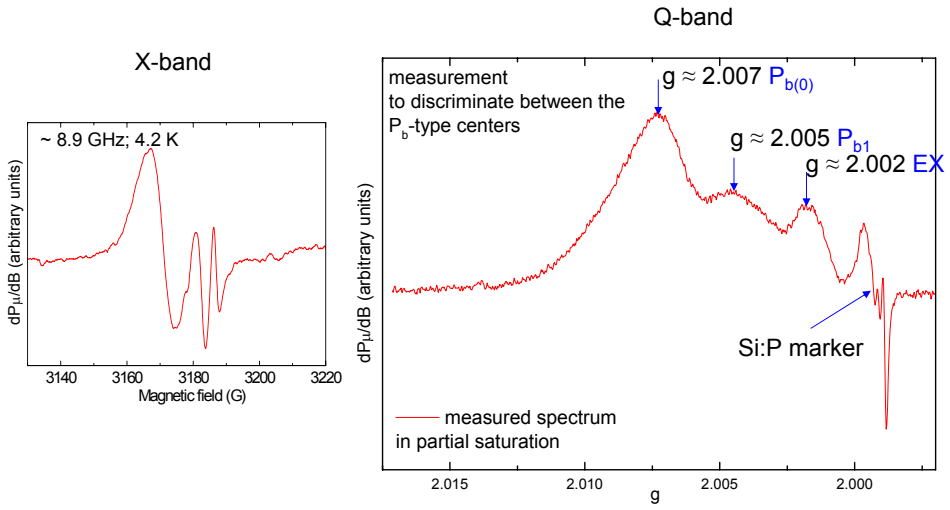



$P_b$-type defects are present in the *as-received* sample (1100 °C)

No discrimination between $P_b$-type defects yet possible.

## ESR aditional measurements

Different frequencies



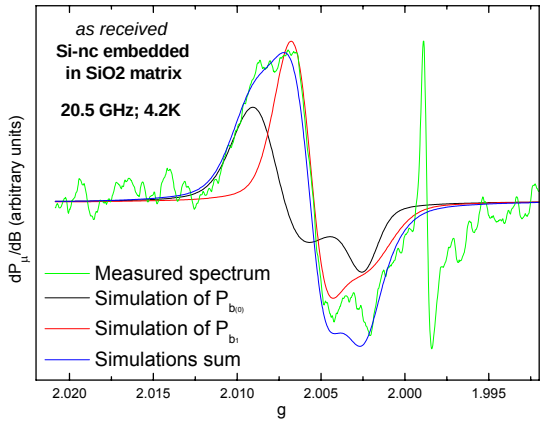

**Low-power first harmonic mode**

**High-power second harmonic mode**



## ESR results
signals simulation

$P_b$-type defects

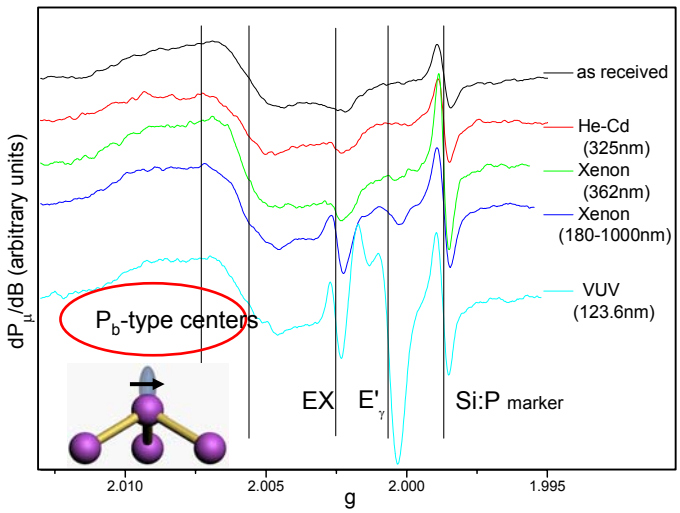



- $P_{b(0)}$, $P_{b1}$ powder patterns
- No evidence for D-line (disordered Si)

The spheric-like Si nc's are bordered by facets of various crystalline orientations (e.g., (111), (100), (110) $Si/SiO_2$), so all the $P_b$-type defects *do co-occur* at the nc-$Si/SiO_2$ interface

## ESR results

*Si/SiO$_2$ interface* specific defects




- Density of $P_b$-type defects do not change detectably =>

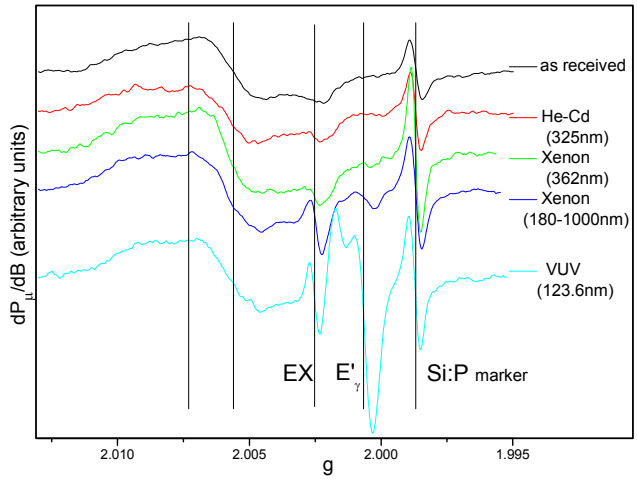
No atomic H

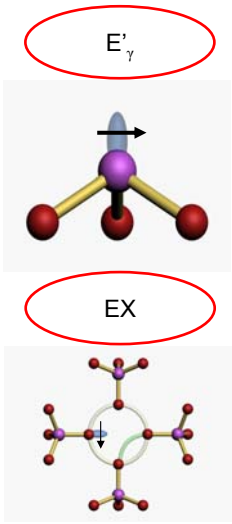
- Appearance $SiO_2$ related defects



## ESR results

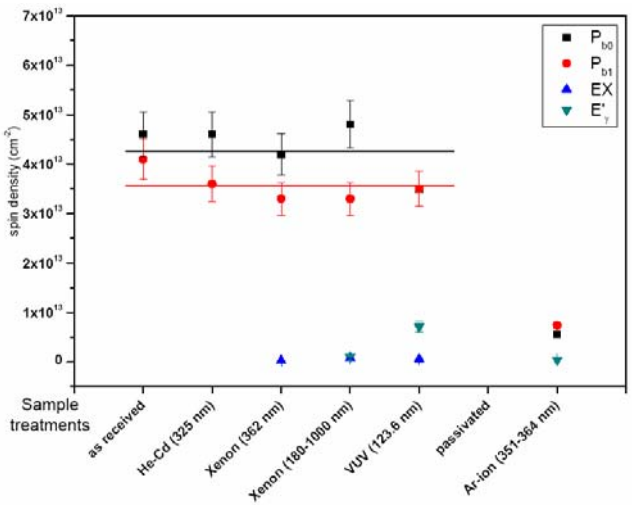
bulk *a-SiO$_2$ specific* defects



## ESR results

review histogram




*as received:*
1 $P_b$-type defect
every **1.4** Si-nc

*passivated + irradiated:*
1 $P_b$-type defect
every **8.6** Si-nc

$P_b$ density comparable to that for regular thermal $Si/SiO_2$

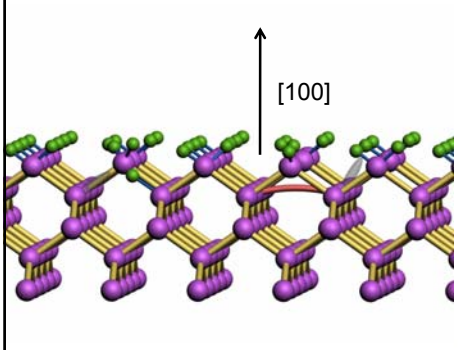


## Outline

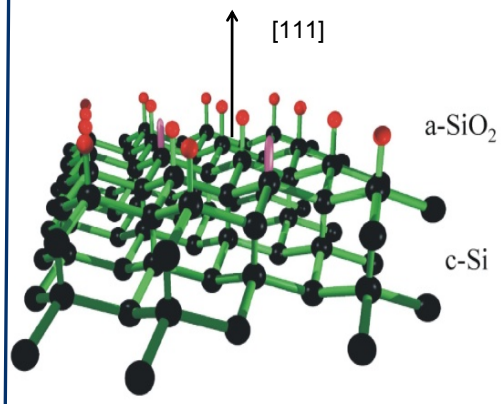
1. ESR active interface defects
2. $Si/SiO_2$ superstructures
3. ESR results
– as received sample
– irradiated sample
– passivated sample
– Ar-ion laser irradiation
4. Morphology
5. Conclusions

## Morphology

interfaces




$P_{b0}$ &$P_{b1}$

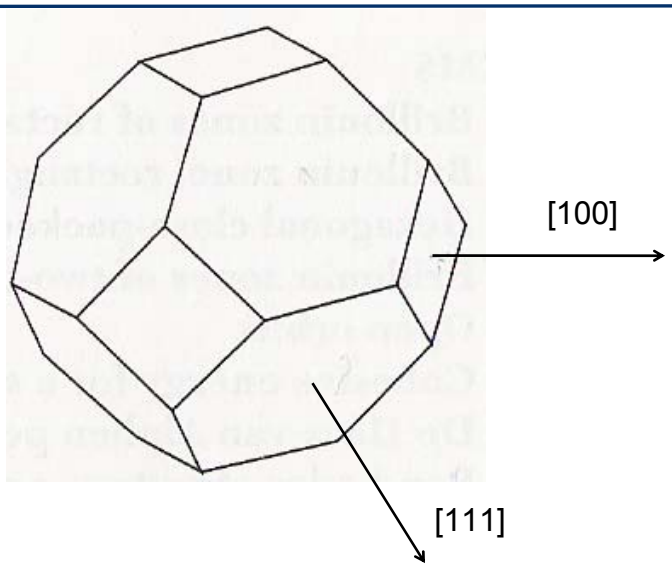



$P_b$



## Morphology

we are proposing a model



## Outline

1. ESR active interface defects
2. $Si/SiO_2$ superstructures
3. ESR results
   – as received sample
   – irradiated sample
   – passivated sample
   – Ar-ion laser irradiation
4. Morphology
5. Conclusions

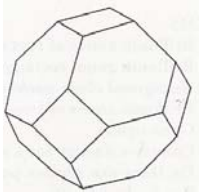


## Conclusions

- Low-T ESR has enabled ***identification*** and ***location*** of naturally occurring point defects in nc-$Si/SiO_2$ superstructures: $P_{b(0)}$, $P_{b1}$, EX and $E'_\gamma$
- $P_b$–type centers density at nc-$Si/SiO_2$ interface is comparable to that for regular thermal $Si/SiO_2$

  ~one every 1.4 Si-nc; mixture of $P_{b(0)}/P_{b1}$
- No evidence for D-line (distorted Si) => mostly crystalline Si-particles.
- Si nc's are bordered by different facets of predominantly 2 crystalline orientations – (111), (100) – so all the $P_b$-type defects do co-occur at the nc-$Si/SiO_2$ interface.
- Morphology:

Propose: **truncated (111) octahedron** model for nc-Si



## Collaboration within INPAC

ESR together with high magnetic field photoluminescence (WP1)

helped solve the origin of

room temperature photoluminescence of nc-Si